

Recovery of Platinum Group Metals from High Level Radioactive Waste

POSSIBILITIES OF SEPARATION AND USE RE-EVALUATED

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When nuclear fuel is irradiated in a power reactor a wide range of chemical elements is created by the fission of uranium and plutonium. These fission products include palladium, rhodium and ruthenium, and could in principle constitute a valuable source of these three metals. Their separation from the fuel during reprocessing operations is, however, a complex matter. Various processes have been proposed and evaluated, mainly on a laboratory scale. To date none of them has been established as applicable on a commercial scale, but investigations with this aim are continuing in several countries. Even a complete separation of the platinum group metals from other nuclides would yield a radioactive product, because of the presence of active isotopes of the platinum group metals. These would be expected to restrict the practical utilisation of platinum group metals created by nuclear fission, unless an isotope separation technique can be developed, or the metals are stored until the radioactivity has decayed.

The irradiation of nuclear fuels in power reactors leads to the production of atoms of a wide range of fission products, ranging in atomic mass from 70 to 160. These fission products generally constitute components of the radioactive waste generated by the nuclear fuel cycle. They include three of the platinum group metals, namely palladium, rhodium and ruthenium, which are valuable because of their scarcity and their strategic importance.

It is the purpose of this paper to review the quantities of the platinum group elements produced (frequently termed the arisings) during nuclear power generation, to describe their behaviour within the fuel cycle, and to consider the feasibility of separating them from suitable waste streams and utilising them industrially.

The question of whether these metals might be separated from nuclear wastes was considered in the early days of the nuclear industry, and interest in it has re-emerged at intervals since then. The topic was previously

reviewed in *Platinum Metals Review* in 1970 (1). The current revival of interest has resulted partly because of the increasing economic importance of rhodium. This metal is a crucial component of the three-way catalysts used for automobile emission control, and the demand for it is therefore strong. However, rhodium is mined in conjunction with platinum and its supply is therefore linked to that of platinum. Increases in the price of rhodium over the last few years have led to renewed interest in possible new sources. For this reason, the present paper concentrates on recent technological developments that might have a bearing on the separation of rhodium from nuclear waste.

Production of Platinum Metals in Nuclear Fuel

Palladium, rhodium and ruthenium are produced in irradiated fuel at fission yields of a few per cent. The quantities produced depend on the type of reactor system and on the burn-up

Table I
Composition of Fission Product Platinum Group Metals
after Cooling for Five Years

| Isotope | Content, weight per cent | Half-life | Specific ^(a) activity, Ci/g metal | Decay mode |
|--------------------|--------------------------|-------------------------|--|----------------------------------|
| Ruthenium | | | | |
| 99 | trace | stable | | |
| 100 | 4.2 | stable | | |
| 101 | 34.1 | stable | | |
| 102 | 34.0 | stable | | |
| 103 | trace | 39 days | Low | $\beta\gamma$ |
| 104 | 23.9 | stable | | |
| 106 | 3.8 | 368 days | 8 | Low energy β |
| Rhodium | | | | |
| 102 | trace | 2.9 years | 1.3×10^{-3} | γ , electron capture |
| 102m | trace | 207 days | 3×10^{-5} | $\beta\gamma$, electron capture |
| 103 | 100 | stable | | |
| 106 ^(b) | trace | 30 seconds | (8) | $\beta\gamma$ |
| Palladium | | | | |
| 104 | 16.9 | stable | | |
| 105 | 29.3 | stable | | |
| 106 | 21.3 | stable | | |
| 107 | 17.0 | 6.5×10^5 years | 5×10^{-5} | Low energy β |
| 108 | 11.7 | stable | | |
| 110 | 3.8 | stable | | |

(a) 1 Curie (Ci) = 3.7×10^{10} Becquerel

(b) ¹⁰⁶Rh exists in secular equilibrium with ¹⁰⁶Ru, and decays rapidly to ¹⁰⁶Pd

to which the fuel is taken, that is the thermal energy generated by fission by unit mass of fuel. In a commercial light water reactor at a burn-up of 33GWd/te about 4 kg of platinum group metals are produced per tonne of heavy metal in the fuel. In a fast breeder reactor, because of the higher burn-up (about 100GWd/te) and the different neutron spectrum, about 19 kg of platinum group metals per tonne are produced. For light water reactor fuel, the approximate composition of the platinum group metals fraction is: palladium 33, rhodium 11 and ruthenium 56 per cent.

Rhodium, currently the most valuable of the three, is generated in the lowest yield.

The isotopic composition of the fission derived platinum group metals is different from that of the natural metals; and it varies over time as the fuel cools, because the radioactive isotopes present are subject to decay. At the time of discharge from the reactor a number of very short lived isotopes are present, but these decay rapidly. The composition after about five years is shown in Table I. With longer times the composition and the total masses of the elements present do not vary significantly,

apart from the conversion of ^{106}Ru to ^{106}Pd .

Some of the isotopes shown in Table I are only present at low mass concentrations, but they are important because they impart radioactivity to the metal. This radioactivity has important implications for the potential utilisation of the metals, even if they were separated. We shall return to this point later in the paper.

In order to obtain an idea of the potential platinum group metals resource in nuclear fuel, it is necessary to consider the size of present and future nuclear power programmes. It is possible to estimate the total world arisings of fission product platinum group metals from their fission yields and the expected arisings of spent fuel based on forecasts from the Organisation for Economic Co-operation and Development (OECD) and others. Light water reactor data can be used for the calculation because this type of reactor will dominate the nuclear power programmes for the world as a whole. In Table II the arisings based on one set of assumptions (2) are compared with annual consumption in the World Outside Centrally-Planned Economies Area (WOCA), and with 1982 estimates of the world reserves. Full details of the calculations are given elsewhere (2).

The data show that nuclear arisings of the platinum group metals are potentially a significant fraction of reserves, and represent many years consumption at current rates. However, the platinum group metals content of the fission product of spent fuel is not immediately available to man. For the metals to become attainable it is necessary for the fuel to be reprocessed. It is thought likely that about half the nuclear fuel from power reactors worldwide will be reprocessed (2).

Behaviour of Platinum Group Metals during Fuel Processing

When spent nuclear fuel is reprocessed, the fuel pins are sheared into short lengths, and the fuel is dissolved away from the cladding into 7M nitric acid. During this operation, the uranium and plutonium oxides that are present dissolve, as do most of the fission products.

There is, however, an insoluble residue which contains some of the platinum group metals. The acid solution is clarified and then passes to a sequence of solvent extraction contactors in which separation of uranium and plutonium from the fission products, and from each other, is carried out. Most of the fission products in the dissolver solution, including the platinum group metals, pass to the aqueous raffinate from the first solvent extraction cycle. This raffinate is subsequently concentrated by evaporation to give high level waste liquor, which is then stored prior to vitrification and final disposal. During these stages further precipitation of insoluble material can occur.

Insoluble Residues

The insoluble material from the dissolution stage contains 70 to 90 per cent fission products, together with miscellaneous residues and traces of undissolved actinides. These fission products exist as metallic alloys containing molybdenum and technetium as well as palladium, rhodium and ruthenium. About 4 to 5 kg of residues per tonne of fuel have been found in small scale tests, and fine material ($<50\ \mu\text{m}$) is present. The amounts and compositions are variable, and the residues are intensely radioactive, with heat outputs of up to 1W/g.

The fraction of the initial inventory of platinum group metals which occurs in the insoluble residues depends on the burn-up to which the fuel has been taken. For high burn-up fast reactor fuel, about 98 per cent of the total expected ruthenium has been found in the residues (3).

The insoluble residues are difficult to treat chemically because of their inertness, and their high radioactivity adds to the difficulty and expense of processing them. Direct high temperature chlorination, or alloying with tin, has been used to bring the residues into solution for analytical purposes (4). It is unlikely, however, that such methods could be scaled up economically.

High temperature processes that are based on extraction with liquid metals have been proposed. For example, molten uranium/chromium or

uranium/iron eutectics extract ruthenium selectively from a solution of the residues in molten magnesium (5). More recently, Japanese investigations have shown that treatment of the residues with lead and a glass-forming material causes extraction of the platinum group metals together with technetium and molybdenum, into the lead phase, leaving other impurities in the glass (6).

Recovery from High Level Liquid Waste

For thermal reactor fuel, which is the commonest type, about two thirds of the platinum group metals are found in the high level liquid waste, and various methods have been suggested for their separation and recovery. The range of the chemical elements present in high level liquid waste spans most Groups in the Periodic Table and the chemical problems of separation are in themselves difficult. Constraints are imposed by the presence of nitric acid (3M in the raffinate). In addition the solutions are radioactive and can only be processed in heavily shielded, and therefore expensive, plant. If the products are to be suitable for general use the separation from other radioactive fission products, for example, caesium-137 must be essentially complete. The platinum group metals also have intrinsic radioactivity of their own, and the implications of this will be discussed later. These factors will make it very difficult to devise an economic separation route, even at the relatively high market values of the platinum group metals. Over the past three decades, several approaches have been suggested in the literature, but none of them has yet demonstrated the potential for application on a commercial scale. In the following paragraphs some recent advances in separation technology that might be applied to the problem are briefly discussed.

Ruthenium

Ruthenium can be separated from other metals in nitric acid solutions by oxidising it to the volatile tetroxide, for example with potassium periodate (2). From the data in

Table I, it is clear that ruthenium-106 and its daughter rhodium-106 are the main contributors to the radioactivity of the platinum group metals fraction. The separation of ruthenium from rhodium and palladium might therefore be a worthwhile objective, perhaps as a preliminary step to the purification of the rhodium and palladium. It would be difficult, however, to achieve the necessary radiochemical decontamination by an oxidative distillation process.

Solvent Extraction Methods

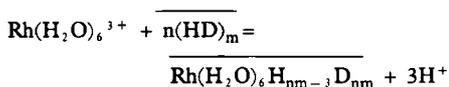
Solvent extraction methods could have potential for the extraction of rhodium and palladium. The selection of suitable extraction reagents requires consideration of the speciation and co-ordination chemistry of these metals in nitric acid solutions. Patel and co-workers have studied rhodium speciation in nitric acid solutions (7). Hydrated cations, principally $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$ are typically present, but in the presence of nitrite ion successive substitution of the water ligands can occur, giving species of the general formula $[\text{Rh}(\text{H}_2\text{O})_{6-n}(\text{NO}_2)_n]^{(3-n)+}$ and ultimately the hexanitrito complex $[\text{Rh}(\text{NO}_2)_6]^{3-}$. Anionic species would be expected to be extracted by basic extractants such as amines, and Beer has demonstrated efficient and rapid extraction of rhodium by long-chain aliphatic amines from nitrite/nitric acid systems in the presence of salting-out reagents (8).

Amine extractants, however, are generally used in the acidity range pH 2–4. In contrast, high level waste contains 1.5 to 3M nitric acid, and its neutralisation before treatment would pose additional process problems.

More recently Davis and co-workers have extracted palladium with a good degree of selectivity from synthetic fission product solutions in 3M nitric acid, using the tertiary amine Alamine 336 in tributyl phosphate/kerosene (9).

Other systems for rhodium extraction have also been reported but suffer from various disadvantages. For example, a hydrocarbon solution of the cation exchanger

dinonylnaphthalene sulphonic acid can be used as an extractant (10); backwashing is readily achieved with nitric acid or with a nitrite solution.



Note: Bar lines indicate species in the organic phase; HD represents dinonylnaphthalene sulphonic acid.

The extraction mechanism here depends not on ligand exchange, which is generally slow for rhodium, but on inclusion in the micelle structures formed by association of the extractant in the hydrocarbon phase. Rhodium extraction is therefore rapid, but the reagent is not selective for rhodium.

Better selectivity for noble metals can be obtained with extractants containing "soft" donor atoms, such as sulphur. The extraction of palladium (11) and rhodium (12) by dialkyl sulphides is well known; but equilibration times for extraction are long (a few hours) making these extractants unsuitable for continuous counter-current solvent extraction processes.

Substituted phosphine sulphides are another potentially useful class of reagents. Alkyl phosphorothioic triamides, $(\text{RNH})_3\text{PS}$, extract a variety of metals, including palladium (13), from mineral acid solutions. For rhodium

extraction from nitric acid media by the reagents R_3PS , when R = phenyl, butyl or $\text{C}_6\text{H}_{13}\text{NH}$, a fairly polar diluent, such as heptanol, is required; extraction is most efficient for the case where $\text{R} = \text{C}_6\text{H}_{13}\text{NH}$ and at 2 to 3M nitric acid; and equilibration times are long (3 to 6 hours) (14). The last of these factors suggests the need for a batch extraction process, rather than continuous counter-current extraction, but the efficiency is not high enough to allow a satisfactory recovery by such a method. Tertiary phosphine sulphides (15) and oxides (16) have also been used to extract palladium.

By careful choice of conditions, solvent extraction, with a sulphur based extractant, might be used to separate rhodium and palladium from high level liquid waste, but selectivity would be difficult to achieve. The processes would tend to be relatively complex, and plant costs would inevitably be high because of the shielding and remote handling equipment required for dealing with the fission product solutions. None of the processes discussed can currently be regarded as economically viable candidates for industrial use.

Utilisation of Fission-Derived Platinum Group Metals

If a perfect chemical separation of the platinum group metals from other fission products and from each other could be carried out,

| Fission product arising | Ruthenium | Rhodium | Palladium |
|-----------------------------------|-----------|---------|-----------|
| 2000 | 364 | 71 | 218 |
| 2030 | 1423 | 280 | 850 |
| Natural reserves (1982) | 3220 | 770 | 8520 |
| Annual consumption in WOCA (1986) | 7.4 | 8.4 | 92.0 |

the products obtained would still be radioactive because of the presence of active isotopes of the metals themselves, see Table I. This fact places severe restrictions on where and how the separated metals might be used, because of the obvious need to limit radiation doses to workers and to the general public. There is also a danger that if the radioactive metals from fission sources became mixed with material from natural sources, for example during metal recycling processes, the whole inventory of these naturally occurring metals could become contaminated with radioactivity.

Ruthenium

Ruthenium separated after cooling for five years would contain 3.8 per cent of ^{106}Ru , giving it a specific activity of 8 Ci/g. ^{106}Ru is a low-energy β emitter, but its daughter ^{106}Rh emits high-energy γ rays and has a half-life of 30 seconds. Whenever ^{106}Ru is present, an equal activity of ^{106}Rh exists in equilibrium with it. Such ruthenium is clearly not suitable for widespread application. The metal would become essentially inactive after cooling for 30 to 50 years, but this long wait would involve economic penalties.

Ruthenium is the lowest priced of the three platinum group metals under consideration (17). It is used mainly in electrical applications and as an electrode material. It is not feasible that fission product ruthenium will be separated and used unless there is a dramatic change in the present situation.

Rhodium

Rhodium is an essential component of three-way catalyst systems for the control of automobile exhaust emissions, an application which accounts for 70 per cent of rhodium usage. Expanding demand for this application has led to steep rises in the price of rhodium.

This situation makes rhodium an attractive candidate for separation. In the complete absence of ruthenium, rhodium would be free of ^{106}Rh . However, the isotopes ^{102}Rh and $^{102\text{m}}\text{Rh}$, although insignificant in mass terms, are sufficient to give separated rhodium a

specific activity which is too high for general use in the motor industry, see Table I. A cooling period of about 50 years would remove the activity. Alternatively, isotopic separation processes could be considered.

Even at the high market value of rhodium, economic separation and use of fission-derived material does not appear likely with the currently available technology.

Palladium

The half-life of the active palladium isotope present in the fission-derived metal is so long (0.65 million years) that its activity is effectively permanent.

In addition, palladium is not as rare as the other platinum group metals, Table II, and currently it is relatively modestly priced (17). For these reasons its separation from high level liquid waste will tend to be unattractive.

Conclusion

The quantities of the three platinum group metals, palladium, rhodium and ruthenium, present in irradiated nuclear fuel are sufficient to constitute a useful resource of these important metals. This is particularly true of rhodium, which is currently of great strategic and economic importance because of its use in vehicle exhaust emission control catalysts.

Progress has been made on the development of chemical methods for extracting the platinum group metals from nuclear waste, but the chemical complexity and high radioactivity of the materials involved make it very difficult to devise an economically attractive process.

Even if completely separated chemically from other fission products, platinum group metals derived from nuclear fuel would remain intrinsically radioactive. This would place a severe restriction on their utilisation, unless they were first stored for a period of say 50 years to allow the activity to decay sufficiently.

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Platinum Silicide Temperature Detectors

During the plasma etching of wafers, the detection of the end-point is important; in a system comprising polycrystalline silicon layers on a silica/silicon substrate this can be indicated by the temperature. The use of an infrared charge-coupled-device, consisting of a 320×244 platinum silicide Schottky barrier detector array, with associated equipment, for thermal imaging has been reported by V. Patel, M. Patel, S. Ayyagari, W. F. Kosonocky and D. Misra of the New Jersey Institute of Technology and B. Singh of the David Sarnoff Research Centre (*Appl. Phys. Lett.*, 1991, **59**, (11), 1299-1301).

The platinum silicide infrared imager is operated at 30 frames/second, and can detect radiation in the 3 to 5 μm spectral range.

The results from the platinum silicide Schottky barrier detector array were compared to those from the commonly used laser interferometry technique for thickness monitoring. It was found that the end-point for etching the polycrystalline silicon could be readily detected, and that the increase in the infrared signal after the silica etching was complete was caused by the heat of the exothermic reaction associated with the etching of silicon in the plasma medium, of carbon tetrafluoride and 15 per cent oxygen at a total pressure of 25 mTorr.

The etch rates for polycrystalline silicon and silica were estimated to be 2100 and 1040 $\text{\AA}/\text{min}$, respectively.

Thus, in addition to end-point detection, thermal imaging can be used for remote wafer temperature sensing, a critical parameter, affecting the etch rate and uniformity, the anisotropy, selectivity, and photoresist integrity.

Palladium Contact Materials

The development of a process that enables palladium-nickel alloy films of accurately controlled composition to be electrodeposited has been reported by scientists at AT&T Bell Laboratories, Murray Hill, New Jersey, (J. A. Abys, H. K. Straschil, I. Kadija, E. J. Kudrak and J. Blee, *Metal Finish.*, 1991, **89**, (7), 43).

The formulation of the bath depends upon the intended plating operation and the alloy required. While temperature, pH, current density, and solution agitation all influence the composition of the electrodeposit, the key factor is the palladium:nickel ratio of the bath. The bath is generally operated at about 35°C, and at a neutral to slightly alkaline pH.

Deposits range from 10 to 30 weight per cent nickel. They have excellent appearance and bulk thermal stability; they are very ductile, harder than hard gold and low in contaminants.